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Computational model for carbon diffusion and methane formation in a ferritic steel during hydrogen attack

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Abstract

Hydrogen attack is a material degradation process which involves partial dissolution of the microstructure in favor of the growth of methane-filled cavities. The various physical–chemical processes involved are strongly coupled. We present a numerical microstructural model for two of these processes, based on a variational approach. © 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Steel; Bulk diffusion; Kinetics; Computer simulation; High temperature corrosion

1. Introduction

Reactors which are exposed to a high hydrogen pressure and to elevated temperatures often suffer from the material degradation process called hydrogen attack (HA). During HA, carbon in the steel reacts with hydrogen that has diffused in from the gas atmosphere inside the reactor, to form methane. These molecules are captured in cavities which have nucleated at the grain boundaries. Due to the presence of methane and hydrogen molecules, the cavities are internally pressurized. Consequently, the cavities grow and coalesce which finally results in intergranular fracture.

The lifetime of a reactor is mainly determined by the cavity growth rate, which is very sensitive to the level of the methane pressure. Several interacting processes are involved in building up the methane pressure, including diffusion of C and of the metal atoms, dissolution of carbides, as well as reaction of C with H to methane inside the growing cavities. Nevertheless, estimates of the lifetime under HA in the literature have decoupled some of these processes by assuming that the methane pressure in the cavity is at its equilibrium value [1–3]. This allows to develop models to predict the HA lifetime of components on the basis of direct material data (e.g. [2]), but the accuracy of these predictions depends sensitively on whether or not the methane pressure is indeed constant. Therefore, we are working on a more detailed modeling of the coupled processes, which will combine continuum mechanics with diffusion, solid solution thermodynamics, kinetics and chemistry.

Previously, a one-dimensional (1D) model has been presented in [4] which takes into account

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these processes within the framework of a multi-component, multi-phase continuum description. Calculations have shown that cavity growth and methane generation are strongly coupled, and that the methane pressure is indeed not constant during exposure. Although the 1D model captures a number of important aspects of the coupled processes taking place during HA, it is based on a number of simplifying assumptions. Among these, are the fact that variations in spatial concentration are ignored and that the spatial positions of carbides relative to the cavity are not resolved. The quantitative consequences of these are hard to predict. Therefore we are developing a more sophisticated model where fewer simplifications need to be made and which allows us to check the assumptions of the 1D model. In this new model we will incorporate substitutional and interstitial diffusion in the ferritic volume elements, the chemical reaction at the cavity–ferrite interface, the movement of the carbide–ferrite interfaces due to the dissolution of carbides as well as the creep and diffusional deformation. The total problem is highly non-linear and will be solved by a finite element method with sharp interfaces. As a first step, we have completed the modeling of the diffusion of carbon in the ferritic matrix along with that of the chemical reaction with the help of special interface elements. This is the subject of the present paper.

2. Numerical description of diffusion and chemical reaction

Diffusion is very often described by Fick's law where the gradient of the concentration drives the flow of atoms. Actually, it is the difference in the chemical potential which is the driving force, and our model is based on this view. Application of the model for the vacancy exchange mechanism of diffusion [5] gives the following linear relation between the molar flux $\vec{J}$ (mol/m^2 s) and the gradient in the chemical potential μ_C^α of carbon in the ferritic matrix:

$$\vec{J} = -\frac{a^{t\alpha} y_C^\alpha (1 - y_C^\alpha) D_C^\alpha}{V_m^\alpha RT} \nabla \mu_C^\alpha. \tag{1}$$

Here, V_m^α is the molar volume of ferrite ($V_m^\alpha = 7.3 \times 10^{-6}$ m^3/mol), R is the gas constant and T is temperature. Since the Gibbs free energy and consequently the chemical potential are described with the sublattice model [6], it is more convenient to work with the site fraction y_C^α as measure for the carbon concentration. Therefore, the number of sites $a^{t\alpha}$ on the second (interstitial) sublattice appears in (1); in the case of ferrite, $a^{t\alpha} = 3$. The mobility of C in the ferrite is characterized in (1) by the Einstein relation D^*/RT where the tracer diffusivity D^* is set equal to the diffusion coefficient D_C^α of C in pure iron. This is a simplified description; more complicated mobility parameters, which also depend on the composition, are used in [7].

When methane is formed at the cavity–ferrite interface by $C + 2H_2 \rightarrow CH_4$, the reaction rate $\dot{\xi}$ is defined by

$$\dot{\xi} = \frac{1}{S}\frac{dn_{CH_4}}{dt} = -\frac{1}{S}\frac{dn_C}{dt}, \tag{2}$$

as the number of moles of methane molecules formed per unit of time and per area (S). The reaction rate plays the role of a thermodynamic flux, while the chemical affinity $A = -(\mu_{CH_4} - 2\mu_{H_2} - \mu_C^\alpha)$ corresponds to the driving force for the methane generation. Here, μ_{CH_4} and μ_{H_2} are the chemical potentials of CH_4 and of H_2. Following the usual procedure, we assume a linear relation between $\dot{\xi}$ and A,

$$\dot{\xi} = -L(\mu_{CH_4} - 2\mu_{H_2} - \mu_C^\alpha), \tag{3}$$

with L a phenomenological kinetic coefficient.

We do not work directly with the Eq. (1) through (3). In order to treat all processes within the same framework, we adopt the variational methodology developed by Cocks and Gill [8]. Referring to [8] for background information, we formulate the dual potential ψ and the rate of change of the Gibbs free energy $\dot{G}$ of the system as a function of flux and reaction rate, and combine them in the functional $\Pi = \psi + \dot{G}$. Then, the exact flux and reaction rate are found by minimization of the functional. Limiting our attention for the moment to carbon diffusion and chemical reaction, we find that the functional Π has the form

$$\Pi = \frac{1}{2}\int \frac{V_m^\alpha RT}{a^{t\alpha} y_C^\alpha (1-y_C^\alpha) D_C^\alpha}\vec{J}\cdot\vec{J}\,dV + \frac{1}{2}\int \frac{\dot{\xi}^2}{L}dS + \int \frac{\dot{G}_m^\alpha}{V_m^\alpha}dV + \int \dot{\xi}\left(\mu_{CH_4} - 2\mu_{H_2}\right)dS. \quad (4)$$

The last two terms represent the change of the Gibbs free energy of the ferritic matrix α and the gas phase containing H_2 and CH_4. The sublattice model [6] gives the Gibbs free energy G_m^α for one mole formula unit ferrite. The corresponding thermodynamic parameters, which can be gathered from the literature are listed in [3]. As G_m^α is a function of the site fraction y_C^α, the change of G_m^α due to diffusion and chemical reaction is simply obtained by

$$\dot{G}_m^\alpha = \frac{\partial G_m^\alpha}{\partial y_C^\alpha}\dot{y}_C^\alpha, \quad (5)$$

while $\dot{y}_C^\alpha$ can be expressed in terms of fluxes via the mass balance

$$\frac{a^{t\alpha}\dot{y}_C^\alpha}{V_m^\alpha} = -\mathrm{div}\vec{J}. \quad (6)$$

Furthermore, the reaction rate $\dot{\xi}$ is related to the flux of C atoms at the cavity–ferrite interface by $\dot{\xi} = \vec{J}\cdot\vec{n}$, where $\vec{n}$ is the unit normal to the surface pointing towards the inside of the cavity. Using this to eliminate $\dot{\xi}$, and inserting (5) and (6) into (4), we can express Π entirely in terms of $\vec{J}$.

We now perform a discretization of the ferritic volume and of the reaction surface via finite elements. The flux at any material point in the ferrite, $\vec{J}(x)$, can be determined from the fluxes **J** at the nodes of the finite element via the shape functions **N**: $\vec{J}(x) = \mathbf{NJ}$.The same holds for the fluxes at the cavity–ferrite interface: $\vec{J}(s) = \mathbf{MJ}$, where **M** is the matrix of the shape functions for the surface elements. By applying the variational principle $\delta\Pi = 0$ for variations of the nodal fluxes $\delta\mathbf{J}$, we obtain the system of equations

$$\sum_e \left(\int \frac{V_m^\alpha RT}{a^{t\alpha} y_C^\alpha (1-y_C^\alpha) D_C^\alpha}\mathbf{N}^T\mathbf{N}\mathbf{J}\,dV^e + \int \frac{1}{L}\mathbf{M}^T\mathbf{M}\mathbf{J}\,dS^e - \int \frac{1}{a^{t\alpha}}\frac{\partial G_m^\alpha}{\partial y_C^\alpha}\mathbf{B}^T\,dV^e + \int \left(\mu_{CH_4} - 2\mu_{H_2}\right)\mathbf{M}^T\vec{n}\,dS^e \right) = 0, \quad (7)$$

that we have to solve for the nodal fluxes **J**. The matrix **B** follows from the divergence of the shape functions. The integrals in this expression are evaluated numerically by Gaussian integration.

Knowing the fluxes, the composition of the ferrite can be updated with (6) and explicit time integration. The moles of methane molecules formed per unit time, dn_{CH_4}/dt are obtained by surface integration of (2). This allows us to calculate the methane pressure by

$$p_{CH_4} = \frac{n_{CH_4} RT}{V^{cav} - n_{CH_4} RTC(T)}, \quad (8)$$

where the non-ideal behaviour of methane is taken into account via the temperature dependent coefficient $C(T)$ [3,9]. V^{cav} denotes the volume of the spherical-caps shaped cavity.

3. Results

In this section we present some first results of the new model for a ferritic microstructure exposed to a hydrogen pressure of 18 MPa at a temperature of 530 °C. The simulation is carried out for a 2D unit cell consisting of a ferritic matrix (Fe, C) with a carbon concentration of $y_C^\alpha = 5\times 10^{-5}$ and a cavity of a fixed size. Fig. 1 shows the

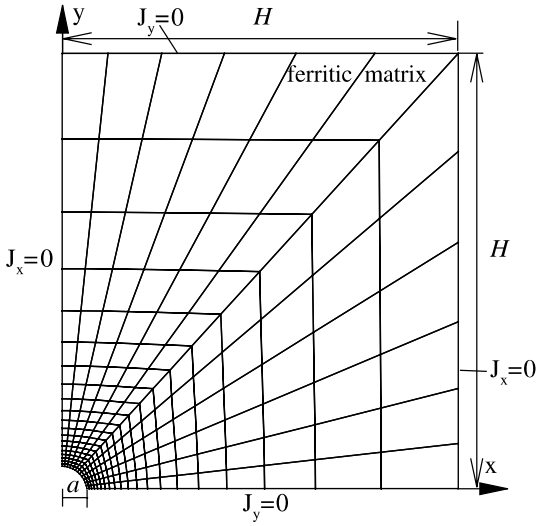

Fig. 1. Quarter of a unit cell for a ferritic matrix with a central cavity.

mesh for a cavity radius $a = 1$ μm with a tip angle $\psi = 78.5°$. Since cavity growth is not accounted for in the new model, we work with a fixed size of the cavity. We consider two cavity sizes: $a = 0.5$ and 1 μm. The 2D unit cell obviously does not represent the geometry of the spherical-caps shaped cavity, but we choose the thickness of the unit cell in such a way that at least the size of the reaction surface corresponds to the size of the spherical-caps shaped cavity. Consequently, the thickness t of the unit cell has to vary with the selected cavity radius via $t = \pi(1 - \cos\psi)a/(\psi \sin\psi)$. As it is reasonable to stick to the same volume of the ferrite per cavity, the dimensions of the unit cell are adapted: the unit cell with the small cavity $a = 0.5$ μm has dimensions $H = 24$ μm and $t = 0.94$ μm, while $H = 17$ μm and $t = 1.87$ μm for the case with $a = 1$ μm.

The kinetic parameter L will depend on the temperature and the hydrogen pressure. Grabke and Martin [10] studied the kinetics of the carburization and decarburization of α-Fe foils in CH_4–H_2 mixtures with a hydrogen pressure up to 0.1 MPa. When we extrapolate their experimental results to our operating conditions, we find that L lies in the range of 10^{-9}–10^{-8} mol^2/J m^2 s. To investigate the influence of L, we perform a parameter study with values for L varying from 10^{-11} to 10^{-8} mol^2/J m^2 s. The diffusion coefficient of C in α-Fe is taken from [11] to be 2.5×10^{-12} m^2/s and $V_m^\alpha = 7.3 \times 10^{-6}$ m^3/mol.

Fig. 2(a) shows the evolution of methane pressure in a cavity of size $a = 0.5$ μm for different values of L. In case of a high value of the kinetic coefficient (i.e. $L = 10^{-8}$ mol^2/J m^2 s), a methane pressure of 745 MPa is reached within 250 s. When we decrease L to 10^{-9} mol^2/J m^2 s, the methane pressure is built up somewhat slower; the maximum methane pressure is reached within 500 s. Decreasing L further to 10^{-10} and 10^{-11} mol^2/J m^2 s, we see a much more pronounced retardation in the methane formation. It takes 3000 s before the ultimate methane pressure is reached in case of $L = 10^{-10}$ mol^2/J m^2 s and 30,000 s in case of $L = 10^{-11}$ mol^2/J m^2 s. Nevertheless, this is a short period compared to the lifetime of a reactor. It seems that in case of $L = 10^{-8}$ and 10^{-9} mol^2/J m^2 s the chemical reaction goes faster than the diffusion of carbon atoms towards the cavity; we are in the diffusion controlled regime. With lower values for L we approach the reaction controlled regime.

To obtain a clearer indication, we consider the dimensionless parameter that describes the competition between the rates of diffusion and chemical reaction. Based on the first two integrals in (7), we find the following dimensionless parameter:

$$\mathscr{L} = \frac{V_m^\alpha RTH^2}{a^{t\alpha} y_C^\alpha (1 - y_C^\alpha) D_C^\alpha} \frac{L}{\psi a} \begin{cases} \ll 1 \ldots \text{reaction controlled} \\ \gg 1 \ldots \text{diffusion controlled} \end{cases} \tag{9}$$

Note that the value of $\mathscr{L}$ evolves during the process as the local value of the carbon concentration changes and when cavity grows. With our material

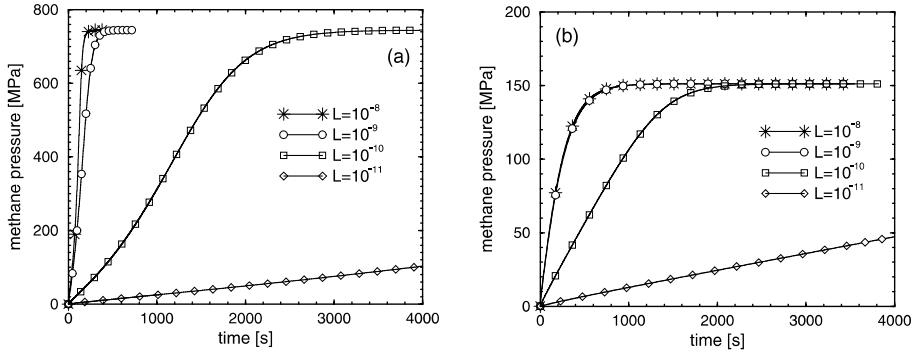

Fig. 2. Development of the methane pressure in a cavity of the radius 0.5 μm (a) and of 1 μm (b) located in a ferritic matrix with the initial carbon composition $y_C^\alpha = 5 \times 10^{-5}$ as a function of the kinetic coefficient L.

parameters and the operation temperature of 803 K we obtain $\mathscr{L} = 10^{11}L$ for $H = 24$ μm and $a = 0.5$ μm when using the value of $y_C^\alpha = 5 \times 10^{-5}$ corresponding to the initial ferritic carbon concentration. The case $L = 10^{-8}$ mol^2/J m^2 s of Fig. 2(a) is characterized by $\mathscr{L} = 1000$, while $\mathscr{L} = 100$ for $L = 10^{-9}$ mol^2/J m^2 s, which both lie in the diffusion controlled regime indeed.

Fig. 2(b) shows the evolution of the methane pressure in the larger cavity ($a = 1$ μm) for the same values of L. To achieve the same methane pressure as in the small cavity, more carbon atoms have to react. This is the reason for a slower kinetics and for a lower methane pressure (151 MPa compared to the previous 745 MPa). The curves for $L = 10^{-8}$ mol^2/J m^2 s ($\mathscr{L} = 270$) and for $L = 10^{-9}$ mol^2/J m^2 s ($\mathscr{L} = 27$) coincide which proves that with these kinetic parameters one is in the diffusion controlled regime. In these cases, the initial carbon concentration $y_C^\alpha = 5 \times 10^{-5}$ decreases by two orders of magnitude to about 7×10^{-7} (see Fig. 3(b)), so that the initial value of $\mathscr{L}$ increases to 19,000 for $L = 10^{-8}$ mol^2/J m^2 s and to 1900 for $L = 10^{-9}$ mol^2/J m^2 s. In case of the low kinetic coefficient $L = 10^{-11}$ mol^2/J m^2 s the maximum methane pressure is reached after 17,000 s.

Finally, we address the distribution of carbon in the ferritic matrix. Our 1D model [4] is based on the assumption of a homogeneous distribution of carbon in the ferritic matrix. The new model allows us to check the validity of this assumption. Therefore, we investigate the evolution of the carbon concentration for the case of $L = 10^{-8}$ mol^2/J m^2 s where the highest concentration gradients can be expected. Fig. 3 shows the concentration profiles along the x-axis of the unit cell at various exposure times for $a = 0.5$ μm (a) and $a = 1$ μm (b). Within a few seconds of exposure, the carbon concentration at the cavity–ferrite interface decreases from 5×10^{-5} to nearly zero and a large concentration gradient is built up in the ferrite. In case of the small cavity (Fig. 3(a)), this gradient is seen to disappear quickly. When the cavity is larger (Fig. 3(b)), a large concentration gradient exists for a longer time. When the methane molecules are formed more slowly due to smaller value of L, more moderate differences in concentration of carbon are obtained. In case of $L = 10^{-9}$ mol^2/J m^2 s the carbon concentration at the interface immediately goes down to a value of 1×10^{-5} for $a = 0.5$ μm and to 1.5×10^{-6} for $a = 1$ μm. In case of $L = 10^{-10}$ mol^2/J m^2 s or smaller, one can speak of a nearly homogeneous distribution of the carbon in the ferritic matrix because the difference in carbon concentration near the cavity and near the outer side of the unit cell is at most 1×10^{-5}. The detailed analysis justifies the assumption of a homogeneous carbon distribution made in our 1D model.

4. Conclusions

The model presented here is part of a sophisticated model which takes into account the processes involved in HA in a coupled manner.

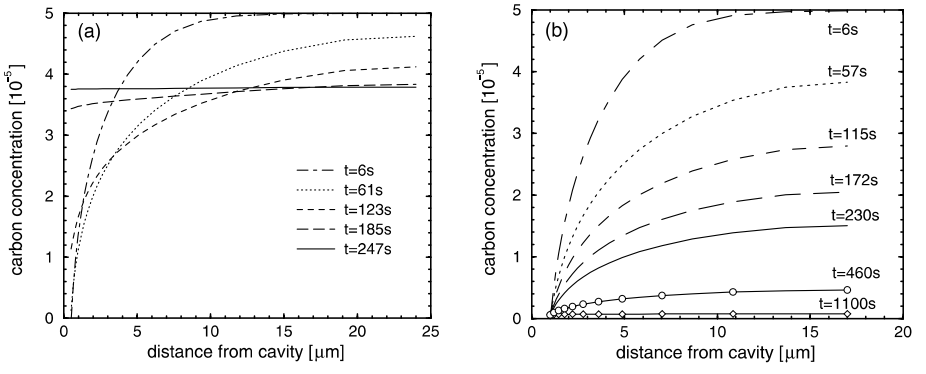

Fig. 3. Carbon concentration as a function of the distance from the cavity center with $a = 0.5$ μm (a) and $a = 0.5$ μm (b) in a ferrite with the initial composition $y_C^\alpha = 5 \times 10^{-5}$ for different exposure times ($L = 10^{-8}$ mol^2/J m^2 s).

Interacting processes are diffusion of metal atoms and carbon in the ferritic matrix, the methane formation, the migration of the carbide–ferrite interfaces and cavity growth. The model presented here deals with the diffusion of C in the ferrite and the chemical reaction of hydrogen and carbon to methane.

An important ingredient is the kinetic coefficient L which relates the reaction rate of methane formation to its driving force. A parameter study has been carried out to investigate the influence of L, and a dimensionless parameter has been derived to quantify whether the reaction or the diffusion of carbon is the rate determining process. For a large value of L we obtain the evolution of the methane pressure for the diffusion controlled range. Without cavity growth being accounted for, the methane pressure in a small cavity is built up within several hundreds of seconds. For lower L, the methane pressure builds up more slowly, i.e. within several thousands of seconds.

These times are obviously much shorter than the lifetime of a reactor. This indicates that one of the processes that has not been incorporated in the present model is the rate determining process in practice. It is likely that this is the diffusion of the substitutional elements which takes place during dissolution of the carbides that are present in real materials. The associated diffusion coefficients are typically 10 orders of magnitude smaller than that of C. The framework presented here is well suited to incorporate the treatment of these processes, and this will be reported in a forthcoming paper.

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